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Recent and emerging applications of holographic photopolymers and nanocomposites

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Abstract. Sensing applications of holograms may be based on effects such as change in the spacing of the recorded fringes in a holographic diffraction grating in the presence of an analyte so that the direction of the diffracted laser light changes, or, in the case of a white light reflection grating, the wavelength of the diffracted light changes. An example is a reflection grating which swells in the presence of atmospheric moisture to indicate relative humidity by a change is the colour of the diffracted light. These devices make use of the photopolymer's ability to absorb moisture.

In a more versatile approach one can add inorganic nanoparticles to the photopolymer composition. These nanoparticles have refractive indices that are different from that of the bulk photopolymer. During the holographic recording of diffraction gratings, the polymerisation and accompanying diffusion processes cause redistribution of the nanoparticles enhancing the holographic diffraction efficiency. Zeolite nanoparticles have the form of hollow cages enabling them to trap analyte molecules of appropriate sizes. The refractive index of the nanoparticle-analyte combination is normally different from that of the nanoparticles alone and this alters the refractive index modulation of the recorded grating, leading to a change in diffraction efficiency and hence of the strength of the diffracted light signal.

Yet another approach makes use of a principle which we call dye deposition holography. The analyte is labelled using a dye which acts as a photosensitiser for the polymerisation process. When the analyte labeled is deposited on a layer containing the other photopolymer components photopolymerisation can take place. If the illumination is in the form of an interference pattern, a diffraction grating is formed, in the region where dye has been deposited. In this way the formation of a holographic diffraction grating itself becomes a sensing action with the potential for extremely high signal to noise ratio.

The method also allows fabrication of photonic devices by direct writing, using photosensitising dye, of structures such as Fresnel zone plate lenses and waveguides onto the photopolymer layer followed by exposure to spatially uniform light.

Our work on HDS is concerned with enhancing the diffraction efficiency of user selected very weak diffraction gratings by illumination with a single beam at the Bragg angle. Light in the illuminating beam is coupled into the diffracted beam and the two interfere to enhance the grating strength. In this way grating diffraction efficiency can be raised above a threshold so that a binary zero can be changed to binary one. A large number of identical weak holographic gratings may be multiplexed into the recording medium at the manufacturing stage, for user selection at the data recording stage. In this way consumer HDS systems could be made much more simply and cheaply than at present.

Keywords: holography, photopolymers, photosensitizing dyes, sensors, holographic optical data storage

PACS: 42.25Fx, 42.25Hz, 42.40Eq, 42.40My, 42.70Ln

PHOTOPOLYMERS

Photopolymer systems for use with visible light normally consist of a sensitizing dye, a co-sensitiser, a monomer and a cross-linking monomer. These components may be held together in a dry layer by means of a binder. The components in our system are usually erythrosin B dye for use at the 532 nm frequency doubled Nd YVO4 laser

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wavelength, triethanolamine as a co-sensitiser, acrylamide monomer, bisacrylamide cross-linking monomer and polyvinyl alcohol binder. Typical compositions have been published[1] including the mechanism of recording. When a layer is illuminated by an optical interference fringe pattern, photopolymerization of acrylamide in bright interference fringe regions reduces the monomer concentration. The resulting monomer concentration gradient causes diffusion of monomer from dark to bright fringe regions. Some diffusion of short chain polymer takes place in the opposite direction to that of monomer diffusion The refractive index thus becomes spatially modulated, mapping the spatial modulation of the interference fringes, and is due to a combination of double to single bond conversion and local density changes. Diffraction efficiencies of as high as 30% have been obtained in reflection holographic diffraction gratings recorded in our photopolymer[2].

Holographic Sensing

Type 1 Sensors

Type 1 sensors are holograms and holographic diffraction gratings in which the polymer rich regions may move further apart by swelling as a result of the absorption of an analyte of which one of the simplest examples is water vapour. A humidity sensor based on this concept in the form of a reflection hologram has been developed and characterized in detail[3,4]. The wavelength at which its diffraction efficiency is maximum, traverses the visible spectrum as the relative humidity changes (see Fig.1) . This type of humidity sensor is reversible, recovering its initial colour when the RH returns to its original value.

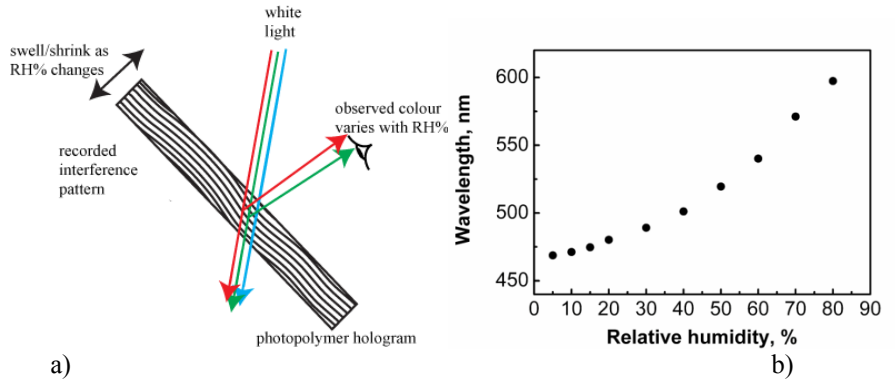


FIGURE 1. Reflection hologram acting as a humidity sensor: a) basic principle b) dependence of diffraction efficiency peak wavelength on relative humidity

It was observed that by a careful choice of the sample thickness and the chemical composition of the layers one can adjust the time response of the sensors [2, 3]. A sensor changes its colour after breathing on it within a few seconds and the time required to return to its initial state can be up to a few minutes. Generally the response time is determined by the thickness

An irreversible version is desirable for some applications but for this we need to adopt a different approach in which zeolite nanoparticles are added to the photopolymer composition. Such particles have a hollow cage like structure and can trap molecules which are small enough to enter them or become attached to them by a form of chemical bonding. They can form stable dispersions in water and have the same pH as the photopolymer host. A range of size, shape and refractive index is available depending on their precise chemical composition. The best performing zeolite nanoparticle dopants in acrylamide-based photopolymers are Si-MFI. Spatially resolved Raman spectraoscopy has shown that redistribution of the nanozeolites takes place during holographic recording (Fig. 2) , the nanoparticles being expelled from bright fringe regions and accumulating in dark fringe regions.

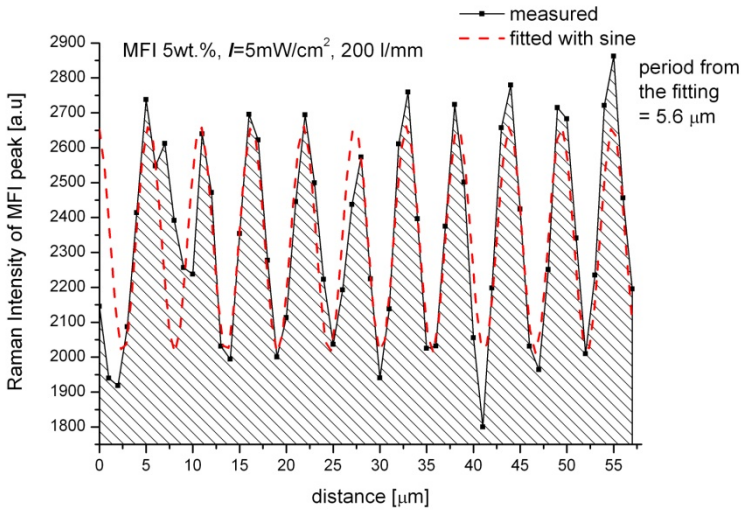


FIGURE 2 Redistribution of MFI zeolite nanoparticles as a result of holographic grating recording

The spatial modulation of polymer concentration is thus accompanied by an out of phase spatial modulation of nanoparticle concentration. Preferential trapping of an analyte by the nanoparticles can alter the refractive index modulation since the refractive index of nanoparticle plus analyte may differ from that of the polymer. This leads to a change in the diffraction efficiency of a holographic diffraction grating.

Once trapped by the nanozeolites, water is retained so that a change in the diffraction efficiency of a transmission grating or in the colour of a reflection grating is permanent (Fig. 3).

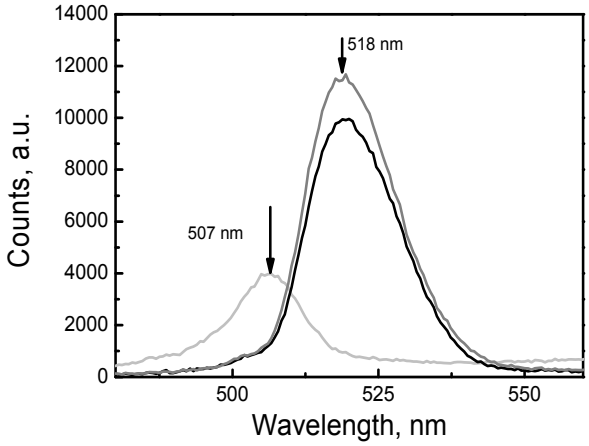


FIGURE 3. Irreversible change of the spectral peak position due to absorption of water in AlPO-18 doped samples. Spectral response at 20%RH - immediately after baking (light gray), after exposure to 80% RH for 200min (black); after 17 hours at 20%RH (mid-gray).

Type II Sensors

In Type II sensors the sensing action consists of the *formation* of a diffraction grating which diffracts a light beam towards a photodetector. The recording material consists only of monomers, a co-sensitiser and the binder. The dye sensitizer is added only when an analyte labeled with the dye is brought into contact with the recording material. The principle is easily demonstrated by depositing dye in the form of text or pictures on dry photopolymer layer which is then exposed to an interference pattern. Diffraction gratings are formed only where dye has been deposited.

A demonstration of type II sensing has been carried out[5]. Single stranded 17- mer DNA molecules were labelled with Eosin-5-isothiocyanate at a concentration of 10 mM. Solutions (0.5 μl) of the dye labelled DNA with concentrations from 10^{-3} to 10^{-9} M were deposited on a premium microarray substrate (ArrayIt, SuperEpoxy 2). Thus

the amount of DNA deposited at each location was between 0.5 nmols to 0.5 fmols. A unsensitised dry photopolymer layer, with normal concentrations of the photopolymer components, was peeled from a microscopic glass substrate, placed in contact with the microarray substrate was and exposed to an interference pattern under normal recording conditions. The result was that diffraction gratings were successfully recorded in the photopolymer layer in those areas which were in contact with the dye labelled DNA. Detection by eye of 50 fmol of DNA was readily obtained by observing, in ordinary white light, the familiar rainbow effect due to the recorded grating. There is considerable scope for improvement in the sensitivity of the method by using dyes with higher triplet yield and by optimizing the other photopolymer component concentrations and the recording conditions, including the spatial frequency of the interference pattern. The advantage here is that the light signal to be detected is a pencil thin beam of laser or LED light confined to a direction determined by the spatial frequency of the recorded interference pattern, thus avoiding the problems associated with collecting fluorescent light, which is the normal detection method.

Dye Deposition Lithography

The fact that polymerization can be spatially localized leads naturally to the possibility of direct deposition of dye under computer control in any desired pattern. Figure 4 shows the concept of direct deposition of dye under positional control of a printing device, which allows for the fabrication of diffractive optical elements.

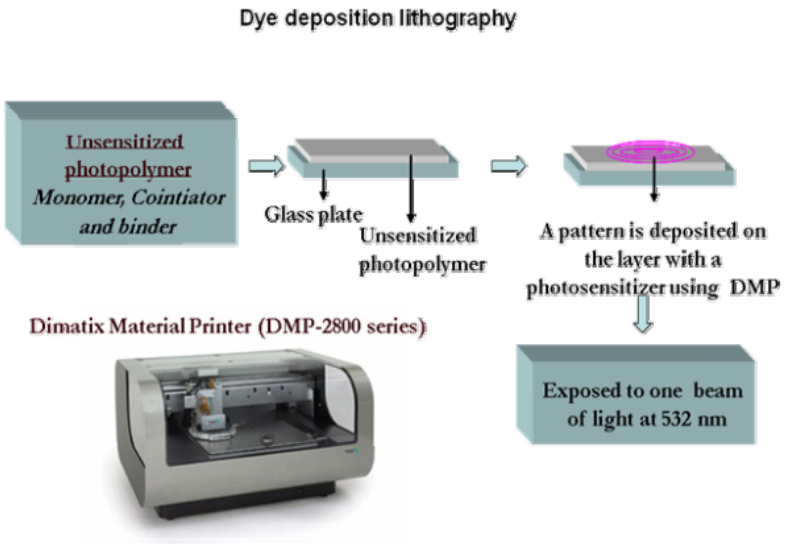
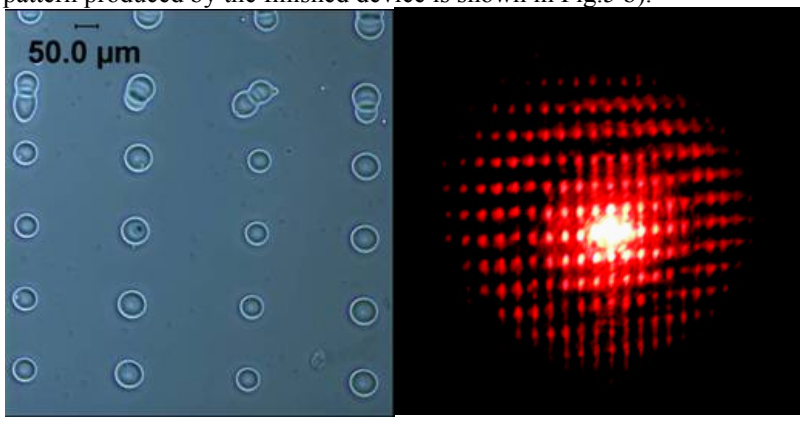

Dye deposition lithography
Unsensitized photopolymer Monomer, Cointiator and binder
Glass plate
Unsensitized photopolymer
A pattern is deposited on the layer with a photosensitizer using DMP
Dimatix Material Printer (DMP-2800 series)
Exposed to one beam of light at 532 nm

Figure 4. Scheme for dye deposition lithography

Figure 5 shows the phase contrast image of a pattern of dye drolets deposited on a dry layer of otherwise inactive photpolymer. On exposure to laser light of wavelength to which the dye is sensitive, photopolymerisation takes place. The diffraction pattern produced by the finished device is shown in Fig.5 b).

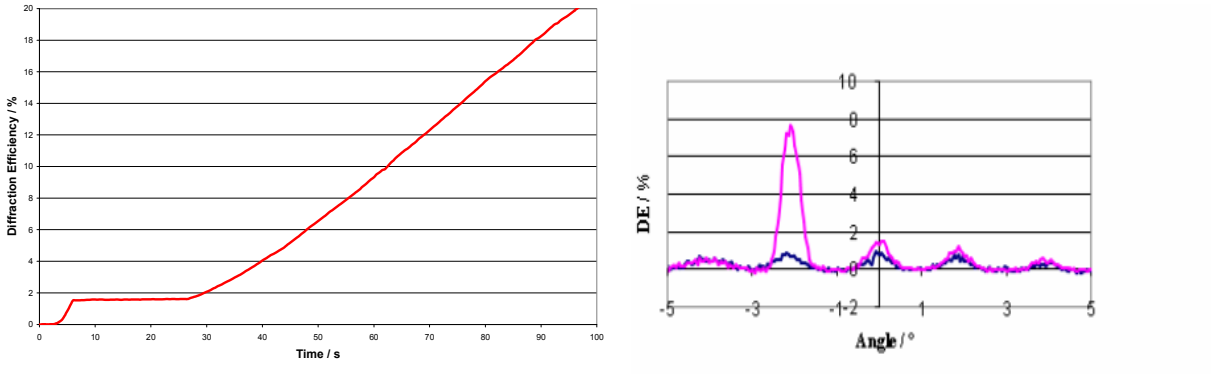


a) b)

FIGURE 5. a) Phase contrast image of a pattern of deposited dye droplets b) resulting diffraction pattern

Single Beam Enhancement of Holographic Diffraction Gratings

In certain photopolymer systems it is found that a holographic diffraction grating of low diffraction efficiency recorded using two beam interference, can be subsequently enhanced using only one of the beams illuminating the grating at the Bragg angle. An example is shown in Fig. 6



a) b)

FIGURE 6 a) Enhancement of the efficiency of a diffraction grating recorded using two beam interference to reach a diffraction efficiency of less than 2%. After a delay of 35 seconds a single beam is used to increase the efficiency to 26%. b) selective enhancement of one of a series of gratings

Delays between two beam and successful single beam recording of up to 28 days have been achieved. Enhanced diffraction efficiencies of well over 80% are possible. The mechanism here is that the weak grating diffracts some of the illuminating light and the two beams interfere, enhancing the grating. Thus the intensity ratio of the two beams is initially very small, typically 0.01 but rapidly tends to 1.0.

The advantages here are 1) only a simple optical setup is required for selective enhancement of gratings 2) there is no need for vibration isolation at the second stage of recording since the interfering beams are confined entirely within the photopolymer layer and 3) the coherence length of the light source required for grating enhancement, is extremely short as path differences are very small within the layer where interference between the weak diffracted beam and the illuminating beam takes place.

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